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A Model System of Reacting H_2 and I_2

by

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We will now consider a model system of reacting H_2 and I_2 at temperature T which is separated by a Knudsen barrier from a similar system at temperature $T + \Delta T$. This system will then have the properties of chemical reaction and transport. The system H_2, I_2 has been studied extensively from the point of view of kinetics. The Knudsen barrier is useful to allow transport without introducing derivatives with respect to distance. For simplicity we take equal volumes of 1 liter on both sides.

We consider the steady state. Let x_1, y_1, z_1 be the concentrations at temperature T of H_2, I_2 and HI respectively. Similarly let x_2, y_2 and z_2 be the concentrations at $T + \Delta T$.

The following six equations are necessary to calculate the concentrations in the steady state:

$$\frac{dx_1}{dt} = 0 = -Ae^{-\frac{E_A}{RT}} x_1 y_1 + A' e^{-\frac{E_A'}{RT}} z_1^2 + K\sqrt{\frac{T + \Delta T}{m_x}}\, x_2 - K\sqrt{\frac{T}{m_x}}\, x_1 \qquad (1)$$

$$\frac{dy_1}{dt} = 0 = -Ae^{-\frac{E_A}{RT}} x_1 y_1 + A' e^{-\frac{E_A'}{RT}} z_1^2 + K\sqrt{\frac{T + \Delta T}{m_y}}\, y_2 - K\sqrt{\frac{T}{m_y}}\, y_1$$

$$\frac{dx_2}{dt} = 0 = -Ae^{-\frac{E_A}{R(T + \Delta T)}} x_2 y_2 + A^{1} e^{-\frac{E_A^{1}}{R(T + \Delta T)}} z_2^2 + K\sqrt{\frac{T}{m_x}}\, x_1 - K\sqrt{\frac{T + \Delta T}{m_x}}\, x_2 \tag{3}$$

$$\frac{dy_2}{dt} = 0 = -Ae^{-\frac{E_A}{R(T + \Delta T)}} x_2 y_2 + A^{1} e^{-\frac{E_A^{1}}{R(T + \Delta T)}} z_2^2 + K\sqrt{\frac{T}{m_y}}\, y_1 - K\sqrt{\frac{T + \Delta T}{m_y}}\, y_2 \tag{4}$$

$$2x_1 + 2x_2 + z_1 + z_2 = 2N \tag{5}$$

$$2y_1 + 2y_2 + z_1 + z_2 = 2N \tag{6}$$

Here N is the number of I_2 moles which is also to be taken as the H_2 moles initially. Also A, E_A are the kinetic constants for the forward reaction and A^{1}, E_A^{1} the kinetic constants for the backward reaction. The constant K depends on the Knudsen barrier such that the number flow per unit area is $\frac{1}{4}\, c\bar{v}$ where c is a concentration and $\bar{v}$ is the average molecular speed.

To simplify the algebra we shall linearize the equations by assuming that we are close to equilibrium. Thus for equilibrium we have

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{z^2}{xy} = \frac{Ae^{-\frac{E_A}{RT}}}{A^{1}e^{-\frac{E_A^{1}}{RT}}} \tag{7}$$

If N = total number of I atoms and H atoms on one side

$$2x + z = N \tag{8}$$

$$2y + z = N \tag{9}$$

We obtain

$$z_{eq} = \frac{\sqrt{K_{eq}}\ N}{2[1 + \frac{1}{2}\sqrt{K_{eq}}]} \tag{10}$$

and

$$x_{eq} = y_{eq} = \frac{N}{2} - \frac{z_{eq}}{2} \tag{11}$$

For the reaction studied $K_{eq} = \frac{5}{3} e^{\frac{4000}{RT}}$. We now let $x_1 = x_{eq} + \Delta x_1$, $x_2 = x_{eq} + \Delta x_2$, $y_1 = y_{eq} + \Delta y_1$, $y_2 = y_{eq} + \Delta y_2$, etc. Also we expand the exponential and square root by Taylor expansion. Substituting into equations (1) through (6), we find the following six equations:

$$\begin{aligned}&[Ae^{-\frac{E_A}{RT}} x_{eq} + K\sqrt{\frac{I}{m_x}}]\Delta x_1 + Ae^{-\frac{E_A}{RT}} x_{eq}\ \Delta y_1 \\ &\quad - 2A^{1}e^{-\frac{E_A^{1}}{RT}} z_{eq}\ \Delta z_1 - K\sqrt{\frac{T}{m_x}}\ \Delta x_2 = \frac{K\Delta T}{2\sqrt{Tm_x}}\ x_{eq}\end{aligned} \tag{I}$$

$$\begin{aligned}&Ae^{-\frac{E_A}{RT}} x_{eq}\ \Delta x_1 + [Ae^{-\frac{E_A}{RT}} x_{eq} + K\sqrt{\frac{T}{m_y}}]\ \Delta y_1 \\ &\quad - 2A^{1}e^{-\frac{E_A^{1}}{RT}} z_{eq}\ \Delta z_1 - K\sqrt{\frac{T}{m_y}}\ \Delta y_2 = \frac{K\Delta T}{2\sqrt{Tm_y}}\ x_{eq}\end{aligned} \tag{II}$$

$$\begin{aligned}&[Ae^{-\frac{E_A}{RT}} x_{eq} + K\sqrt{\frac{T}{m_x}}]\Delta x_2 + Ae^{-\frac{E_A}{RT}} x_{eq}\ \Delta y_2 \\ &\quad -2A^{1}e^{-\frac{E_A^{1}}{RT}} z_{eq}\ \Delta z_2 - K\sqrt{\frac{T}{m_x}}\ \Delta x_1 \\ &= A^{1}e^{-\frac{E_A^{1}}{RT}} \frac{E_A^{1}}{RT^2} z_{eq}^{\ 2}\ \Delta T - Ae^{-\frac{E_A}{RT}} \frac{E_A}{RT^2} x_{eq}^{\ 2}\ \Delta T - \frac{K}{2\sqrt{Tm_x}}\ x_{eq}\Delta T\end{aligned} \tag{III}$$

and

$$Ae^{-\frac{E_A}{RT}} x_{eq}\Delta x_2 + [Ae^{-\frac{E_A}{RT}} x_{eq} + K\sqrt{\frac{T}{m_y}}]\Delta y_2$$

$$- 2A'e^{-\frac{E_A'}{RT}} z_{eq}\Delta z_2 - K\sqrt{\frac{T}{m_y}}\,\Delta y_1 \tag{IV}$$

$$= A'e^{-\frac{E_A'}{RT}} z_{eq}{}^2 \frac{E_A'}{RT^2}\,\Delta T - \frac{K}{2\sqrt{Tm_y}} x_{eq}\Delta T - Ae^{-\frac{E_A}{RT}} x_{eq}{}^2 \frac{E_A}{RT^2}\,\Delta T$$

For the equations (8) and (9) we have

$$\Delta x_1 + \Delta x_2 = - \frac{1}{2}(\Delta z_1 + \Delta z_2) \tag{V}$$

$$\Delta y_1 + \Delta y_2 = - \frac{1}{2}(\Delta z_1 + \Delta z_2) \tag{VI}$$

We shall see that in computing total energies either kinetic or internal we shall need the sum of concentrations. In other words we shall need the quantity $\Delta z_1 + \Delta z_2$ which by algebraic manipulation is seen to be:

$$\Delta z_1 + \Delta z_2 = \frac{Ae^{-\frac{E_A}{RT}} \frac{E_A}{RT^2} x_{eq}{}^2 - A'e^{-\frac{E_A'}{RT}} \frac{E_A'}{RT^2} z_{eq}{}^2}{Ae^{-\frac{E_A}{RT}} x_{eq} + 2A'e^{-\frac{E_A'}{RT}} z_{eq}}\,\Delta T$$

$$\equiv \alpha(T)\Delta T \tag{12}$$

It is easily seen that $$\alpha(T) = \frac{\dfrac{E_A}{RT^2} - \dfrac{E_A^{\ddagger}}{RT^2}\, z_{eq}^{\;2}}{Ae^{-\frac{E_A}{RT}}\, x_{eq} + 2A^{\ddagger} e^{-\frac{E_A^{\ddagger}}{RT}}\, z_{eq}}$$

For an exothermic reaction E_A is greater than $E_A^{\ddagger}$ and α is a negative number.

We wish now to calculate now a function L which is defined as

$$L = (\text{Kinetic Energy})_{\text{upon isolation}} - (\text{Kinetic Energy})_{\text{steady state}} \tag{13}$$

In our particular case of T_f is the final temperature which is $T + \Delta T_f$ we have (for a unit volume of one liter):

$$\begin{aligned} L = {} & 2K_x(T_f)x_f + 2K_y(T_f)y_f + 2K_z(T_f)z_f \\ & - K_x(T)(x + \Delta x_1) - K_y(T)(y_1 + \Delta y_1) - K_z(T)(z_1 + \Delta z_1) \\ & - K_x(T + \Delta T)(x_2 + \Delta x_2) - K_y(T + \Delta T)(y_2 + \Delta y_2) \\ & - K_z(T + \Delta T)(z_2 + \Delta z_2) \end{aligned} \tag{14}$$

If we use Taylor expansions, we obtain:

$$L = \left[\begin{array}{l} 2\,\frac{\partial K_x}{\partial T}\,x_{eq} + 2\,\frac{\partial K_y}{\partial T}\,y_{eq} + 2\,\frac{\partial K_z}{\partial T}\,z_{eq} \\ + 2K_x\,\frac{\partial x_{eq}}{\partial T} + 2K_y\,\frac{\partial y_{eq}}{\partial T} + 2K_z\,\frac{\partial z_{eq}}{\partial T} \end{array}\right]\Delta T_f$$

$$- \left[\frac{\partial K_x}{\partial T}\,x_{eq} + \frac{\partial K_y}{\partial T}\,y_{eq} + \frac{\partial K_z}{\partial T}\,z_{eq}\right]\Delta T \qquad (15)$$

$$- K_x(\Delta x_1 + \Delta x_2) - K_y(\Delta y_1 + \Delta y_2) - K_z(\Delta x_1 + \Delta z_2)$$

We must now evaluate the temperature ΔT_f. Since the system is at constant volume, we use the total internal energy. Thus:

$$2\,[U_x(T + \Delta T_f)X_f + U_y(T + \Delta T_f)Y_f + U_z(T + \Delta T_z)Z_f]$$

$$= \Delta Q[2z_f - (z_1 + \Delta z_1) - (z_2 + \Delta z_2)]$$

$$+ U_x(T)(x_1 + \Delta x_1) + U_x(T + \Delta T)(x_2 + \Delta x_2)$$

$$+ U_y(T)(y_1 + \Delta y_1) + U_z(T + \Delta T)(y_2 + \Delta y_2) \qquad (16)$$

$$+ U_z(T)(z_1 + \Delta z_1) + U_z(T + \Delta T)(z_2 + \Delta z_2) \quad .$$

Here ΔQ is the heat of reaction (positive for exothermic). The term containing ΔQ can be written as:

$$\Delta Q[2\,\frac{\partial z_{eq}}{\partial T}]\Delta T_f - \alpha\Delta T \quad .$$

Again using Taylor expansions, we find for ΔT_f.

$$\Delta T_f = U_x(\Delta x_1 + \Delta x_2) + U_y(\Delta y_1 + \Delta y_2) + U_z(\Delta z_1 + \Delta z_2)$$

$$+ \frac{\left[\frac{\partial U_x}{\partial T} X_{eq} + \frac{\partial U_y}{\partial T} Y_{eq} + \frac{\partial U_z}{\partial T} Z_{eq}\right]\Delta T - \alpha \Delta Q \Delta T}{2\frac{\partial U_x}{\partial T} X_{eq} + 2\frac{\partial U_y}{\partial T} Y_{eq} + 2\frac{\partial U_z}{\partial T} Z_{eq} + 2U_x \frac{\partial X_{eq}}{\partial T} + 2U_y \frac{\partial Y_{eq}}{\partial T} + 2U_z \frac{\partial Z_{eq}}{\partial T} - 2\Delta Q \frac{\partial Z_{eq}}{\partial T}} \tag{17}$$

Thus L per unit volume (one liter)

$$L = \left\{ \frac{\frac{\partial \sum_i K_{x_i} X_{i\,eq}}{\partial T}}{\frac{\partial \sum_i U_{x_i} X_{i\,eq}}{\partial T} - 2\Delta Q \frac{\partial Z_{eq}}{\partial T}} \right\} \alpha \Delta T \left[U_z - \frac{U_x + U_y}{2} + \sum_i \frac{\partial U_{x_i}}{\partial T} \frac{X_{i\,eq}}{\alpha} - \Delta Q \right]$$

$$+ \left[\frac{K_x + K_y}{2} - K_z\right]\alpha \Delta T - \sum_i \frac{\partial K_{x_i}}{\partial T} X_{i\,eq}\, \Delta T \tag{18}$$

Looking at order of magnitude terms, we find

$$L \cong -\alpha \Delta T \Delta Q \frac{d \sum_L K_{x_L} X_L}{d \sum U_{x_L} X_L} \cong -\alpha \Delta T \Delta Q \tag{19}$$

Since α is negative for an exothermic reaction we see that L must be positive.

Numerical Evaluation

To evaluate internal energies and kinetic energies, we consider vibration uncoupled from rotation and assume simple harmonic motion for vibration. For a mole we have

$$U_{Translation} = \frac{3}{2} RT \tag{20}$$

$$U_{Rotation} = RT \tag{21}$$

$$U_{Vibration} = RT \frac{x_e^{-x}}{(1 - e^{-x})} \tag{22}$$

where $x = \frac{hw_o}{kT}$ $\quad w_o$ = lowest frequency of oscillator.

For kinetic energy of the vibration, we use a virial theorem argument and take $K_{vibration} = \frac{1}{2} U_{vibration}$. If we take a temperature of 300°K, we have $X_{H_2} = 21.15$, $X_{I_2} = 10.289$ and $X_{HI} = 11.083$. Now looking at $L \cong - \alpha \Delta T \Delta Q$ for the $H_2 + I_2 \rightleftarrows 2HI$ reaction, we find $\alpha = - 5.19 \times 10^{-5} \frac{moles}{CC°K}$ and $\Delta Q(300°K) = 2945 \frac{cal}{mole}$. If $\Delta T = 1°K$

$$L \cong .15 \frac{cal}{cc} .$$

If we have 2 moles of reactants per liter, we then have

$$L \cong 75 \frac{cal}{mole} .$$

This quantity is an appreciable fraction of the heat of reaction even for a one degree difference in temperature.